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Activity of homogeneous and heterogeneous catalysts, spectroscopic and chromatographic characterization of biodiesel: A review

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ABSTRACT

Biofuel has got tremendous attraction for the last decade as an alternative source of energy. Bioethanol and biodiesel are two main products of first generation biofuel. Biodiesel is chemically fatty acid methyl esters prepared from various edible and non-edible oils. It has been used as a substitute to mineral diesel during the last decade. This review is about generation, transesterification, factors affecting transesterification, catalysts (homogeneous and heterogeneous) and physico-chemical characterization of biodiesel by chromatographic and spectroscopic techniques. The alkaline homogeneous catalysts (NaOH or KOH) have been used on commercial scale for production of biodiesel because these are cheap and reaction occurs in less time. The heterogeneous catalysts such as metal oxides, e.g., CaO, MgO, SrO, ZnO, La_2O_3, Mg–Al hydrolalcite have been used for transesterification of vegetable oil due to their easy separation and reuse but these catalysts take more time for completion of reaction. The yield of biodiesel may be affected by alcohol/oil ratio, concentration of catalyst, time required for reaction, temperature free fatty acid moisture. The prepared biodiesel has been characterized by chromatographic techniques like gas chromatography, gas chromatography–mass spectroscopy, high performance liquid chromatography and spectroscopic techniques like nuclear magnetic resonance and infrared spectroscopy.

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1. Introduction

The energy demand of the world is being increased day by day due to more population, industrial development, agricultural sector and transportation. The petroleum fuel has been depleting day by day, so fuel shortage spurred interest in diversifying fuel resources, such as biofuels (biodiesel or ethanol), biomass, and solar energies will have to be wide spread. The production and commercial use of biofuel have been increased since the last decade due to environmental concerns, fluctuating oil prices and future supply constraints. Biofuel industries have been increased in many countries in order to decrease dependence on foreign petroleum oil. However the demerits of biofuel include shortage of food crops particularly in developing countries and high cost of process. Biofuels are a wide range of fuels which are in some way derived from biomass. The term covers solid biomass, liquid fuels and various biogases [1]. Biofuel consists of three main generations, first generation biofuel produced primarily from food crops like sugar cane (bioethanol) and vegetable oils (biodiesel), second generation biofuel produced from non-food biomass such as ligno-cellulosic feedstock materials which include by-products (cereal straws, sugar cane bagasse, forest residues), organic components of municipal solid wastes and dedicated feedstocks i.e., purpose grown vegetable grasses, short rotation forests etc, and third generation biofuel produced from microalgae.

The main concern of this review is about the biodiesel (first generation biofuel). Biodiesel is an alternative fuel formulated exclusively for diesel engines and may be prepared from vegetable oils or animal fat. Chemically biodiesel is a mixture of fatty acid methyl esters (FAMEs) derived from the reaction of triglycerides and methanol in the presence of a catalyst. Biodiesel can be mixed with petroleum diesel in any percentage, from 1% to 99%, which is represented by a number following a B. For example, B5 is 5% biodiesel with 95% petroleum, or B100 is 100% biodiesel, without any petroleum. Biodiesel is biodegradable up to 4 times faster than petroleum diesel and non-toxic. It does not ignite spontaneously under normal circumstances due to its higher flash point. It has a mild, rather pleasant odor in accordance with strict industrial specifications that meets ASTM D6751 standards. The aim of this review is to investigate comprehensively various parameters affecting % age yield of biodiesel, comparison of activity of homogeneous and heterogeneous catalysts used in transesterification and finally techniques which have been used for chemical characterization of biodiesel.

1.1. Generations of biodiesel

There are three generations of biodiesel, first generation biodiesel produced from edible oils such as rapeseed [2] soyabean [3–5], palm [6–9], rocket seed [10] sunflower [11,12] etc. More than 95% of this type of biodiesel has been used on commercial scale in USA and Europe. Second generation biodiesel includes use of non-edible oil such as jatropha, [12–14], jojoba oil [15], pongamia pinnata [16,17], neem oil [18] etc. The seeds of jatropha and pongamia pinnata are more suitable [16,17] due to higher oil contents [18]. This type of biodiesel generation has been extensively investigated over the past few years because edible oil has impact on global market and food security [19]. Third generation biodiesel feedstocks are derived from microalgae. Recent research is focused on microalgae to produce biodiesel [20]. The merits and demerits of all the three generations are listed in Table 1.

2. Transesterification

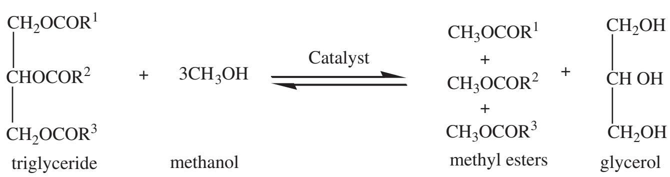
Transesterification, also known as alcoholysis is the reaction of vegetable oil or animal fat with an alcohol to form esters and glycerol. To complete a transesterification reaction, stoichiometrically, a 3:1 M ratio of alcohol to triglycerides is needed. In practice, to have a maximum ester yield, this ratio needs to be slightly higher than the stoichiometric ratio. Because the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side [21]. A catalyst is usually used to improve the reaction

Table 1
Merits and demerits of biodiesels from different generations.

Type of biodiesel generation	Merits	Demerits
First	• Locally grown • High production • Good quality biodiesel	• Require more arable land • Produce serious food and ecological imbalance • Deforestation
Second	• Eliminate food competition • Environment friendly • Require less farm land • Can be cultivated on waste land	• Production is not as per commercial demand • Require more alcohol for transesterification • More viscous
Third	• High photosynthetic efficiency to produce biomass • High growth rate and productivity • Fast reproduction • Better oil % age yield • Do not effect human food supply chain • Do not compete for land with crops used for food production	• Need enough sunshine • Non-availability on commercial scale

rate and yield. The reaction can be catalyzed by alkalis, acids, or enzymes. Generalized reaction is shown in Scheme 1.

Transesterification consists of a sequence of three consecutive reversible reactions. The first step is the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides, and finally monoglycerides to glycerol, yielding one ester molecule for each glyceride at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acids esters and glycerol. The mechanism and kinetics of transesterification have been described in detail by Meher et al. and Encinar et al. [22,23]. The basic mechanism is shown in Scheme 2.



Scheme 1. Transesterification of triglyceride with methanol in the presence of catalyst.

$$\text{Triglyceride} + \text{ROH} \rightleftharpoons \text{Diglyceride} + \text{RCOOR}$$

$$\text{Diglyceride} + \text{ROH} \rightleftharpoons \text{Monoglyceride} + \text{RCOOR}$$

$$\text{Monoglycerides} + \text{ROH} \rightleftharpoons \text{Glycerol} + \text{RCOOR}$$

Scheme 2. General equation for transesterification of triglyceride.

2.1. Experimental process

When the catalyst, alcohol, and oil are mixed, agitated in a reaction vessel, the transesterification reaction will start. A stirred reactor is usually used as the reaction vessel for continuous alkali-catalyzed biodiesel production. The temperature is kept just below the boiling point of the alcohol (i.e. 64.5 °C for methanol). Normally, excess alcohol is used to ensure maximum conversion of the oil to its methyl esters. Once the transesterification reaction is completed, two major products exist, biodiesel and glycerol. The glycerol phase is denser than the biodiesel phase and settles at the bottom of the reaction vessel, allowing it to be separated from the biodiesel phase. Phase separation can be observed within 10 min and can be completed within several hours of settling. The reaction mixture is allowed to settle in the reaction vessel in order to allow the initial separation of biodiesel and glycerol, or the mixture is pumped into a settling vessel. In some cases, a centrifuge may be used to separate the two phases [24]. Both the biodiesel and glycerol are contaminated with the unreacted catalyst, alcohol, and oil during the transesterification step. Soap that may be generated during the process also contaminates the biodiesel and glycerol phase. Schumacher [25] suggested that although the glycerol phase tends to contain a higher percentage of contaminants than the biodiesel, a significant amount of contaminants is also present in the biodiesel. Therefore, crude biodiesel needs to be purified before use.

2.2. Purification of crude biodiesel

After separation from the glycerol phase, crude biodiesel is mainly contaminated with residual catalyst, unreacted alcohol, free glycerol, and soap that were generated during the transesterification reaction [26]. Normally, crude biodiesel is subjected to neutralization step and then passes through an alcohol stripper before the washing step. In some cases, acid is added to crude biodiesel to neutralize unreacted catalyst and to split any soap. Soaps react with the acid to form water soluble salts and free fatty acids. The primary purpose of this step is to wash out the remnants of catalyst, soap, salts, residual alcohol, and free glycerol from the crude biodiesel. Generally, four main approaches are adopted for purification of biodiesel, i.e. water washing, washing with solid adsorbent and water, dry washing [27] and membrane extraction [28–30], which are shown in Table 2 and briefly discussed as follows.

2.2.1. Water washing

Water washing is generally carried out to remove soap, catalyst, methanol and other contaminants from biodiesel. Since glycerol and alcohol are highly soluble in water, water washing is very effective for removing both these contaminants. It also removes any residual sodium salts and soaps. The primary material for water washing is acidified warm water [31,32]. Warm water prevents the precipitation of saturated fatty acid esters and retards the formation of emulsions with a gentle washing action. Acidified water eliminates calcium and magnesium contamination and neutralizes any remaining alkali catalysts [24]. After washing several times, the water phase becomes clear, indicating that the contaminants have been completely removed. Then, the biodiesel and water phases are separated by a separating funnel or centrifugation [33]. Because of the immiscibility of water and biodiesel, molecular sieves and silica gel, can also be used to remove remaining water from the biodiesel [24]. The remaining water can also be removed from the biodiesel by keeping the product over anhydrous Na_2SO_4 (25 wt% of the amount of the ester product) overnight followed by filtration [34,35].

2.2.2. Washing with solid adsorbent and water

Adsorbents are another mean of treating transesterified product. Adsorbent such as magnesol has the potential of selectively adsorbing hydrophilic materials such as glycerol and glycerides. This treatment, followed by filtration, has been shown to be effective in lowering glycerides and total glycerol levels. Some vegetable oils, yellow and brown greases, leave an objectionable color in the biodiesel. Activated carbon bed is used to remove excessive biodiesel color [24]. Dube et al. [36] mentioned the use of solid adsorbents, such as activated clay, carbon, fiber, etc to purify the resultant biodiesel.

Table 2
Merits and demerits of different purification methods for biodiesel.

Approaches	Merits	Demerits	Ref.
Water washing	Very effective in removing contaminants	Increased cost and production time, liquid effluent, product loss, emulsions formation	[30–32,35]
Washing with adsorbent and water	Remove biodiesel color Effective in lowering glycerides and total glycerol level	Problem of wastewater treatment	[36]
Dry washing	Waterless	Over runs the limit in the EN (European) Standard	[37,38]
Membrane extraction	Avoids the emulsion formation and decreases the refining loss	Probably high cost and low throughput due to contaminants	[36,39–41]

Hot deionized water washing at 50 °C is considered to be the best way to separate and purify biodiesel but with challenging wastewater treatment problem.

2.2.3. Dry washing

Ion exchange resin or magnesium silicate powders are being used for dry washing to remove impurities from biodiesel [27]. This method can bring the free glycerol level down and is reasonably effective for removing soaps as well. Both the ion exchange process and the magnesol process have the advantage of being non-aqueous and thus eliminate many problems outlined above. Although the magnesol process has a better effect on the removal of methanol than the ion resins, none of the products from this process fulfill the specified limits in the European Standard (EN) [37,38].

2.2.4. Membrane extraction

The use of membrane equipments for the separation and purification of crude biodiesel seems to exhibit several advantages over the conventional ones such as eradication/minimization of higher capital cost and other related costs of production, and provide high specific area of mass transfer. Membrane equipments for biodiesel refining are usually made from inorganic microporous ceramic membranes. Some of the most effective devices used for the separation and purification of crude biodiesel include: membrane reactor and separative ceramic membrane.

Operations involving membrane technologies in the last years have shown their potentialities in the rationalization of production systems [39]. Membrane performance is usually governed by: selectivity or separation factor and permeability. In the absence of defects, the selectivity is a function of the material properties at given operating conditions. The productivity is a function of the material properties as well as the thickness of the membrane film which is inversely proportional to thickness [40]. Membrane reactors' intrinsic characteristics of efficiency, operational simplicity and flexibility, relatively high selectivity and permeability, low energy requirements, good stability under a wide spectrum of operating conditions, environment compatibility, easy control and scale-up have been confirmed in a variety of applications and operations, as molecular separations, fractionations, concentrations, purifications, clarifications, emulsifications, crystallizations, etc [39].

The membrane reactor removes unreacted vegetable oil from the fatty acid methyl esters (FAMEs) product after transesterification, yielding high-purity biodiesel and shifting the reaction equilibrium to the product side [36]. The membrane process was particularly useful in removing unreacted oil from the FAME product yielding high purity biodiesel. Additionally, a novel refining method using the membrane extraction was developed by He et al. [29]. The authors compared membrane extraction and the traditional extraction methods of biodiesel refining. It is a very promising method for purifying biodiesel.

2.3. Factors affecting the yield of biodiesel

The yield of biodiesel is affected by various factors such as presence of moisture, amount of free fatty acid, molar ratio of alcohol, concentration of catalyst and reaction time. These factors are briefly discussed as follows.

2.3.1. The effects of moisture and free fatty acids

The moisture contents and free fatty acid are key parameters for determining the viability of the vegetable oil for transesterification. The effects of free fatty acids (FFA) and water contents on transesterification of beef tallow with methanol were investigated which showed that the water and FFA content should be kept below 0.06% and below 0.5%, w/w respectively in order to get the best conversion [41,42]. Water content was a more critical variable in the transesterification than were free fatty acids (FFA). The starting materials used for alkali-catalyzed transesterification of glycerides must meet certain specifications. The glyceride should have an acid value less than 1 mg KOH/g of sample and all materials should be substantially anhydrous. If the low qualities of beef tallow or vegetable oil with high FFA are used to make biodiesel fuel, they must be refined by saponification using NaOH solution to remove free fatty acids (FFA). Conversely, the acid catalyzed process can also be used for esterification of these free fatty acids [43–45].

2.3.2. The effect of molar ratio of alcohol

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid alkyl esters and one mole of glycerol. However, transesterification is an equilibrium reaction in which a large excess of alcohol is required to drive the reaction to the product side. Bradshaw and Meuly [43] have reported the practical range of molar ratio 3.3–5.25:1 for methanol to vegetable oil. The ratio of 4.8:1 was used in some examples, with a yield of 97–98%, depending upon the quality of the oils. If a three step transesterification process was used, the ratio was reduced to 3.3:1. Methanol present in amounts of above 1.75 equivalents tended to prevent the gravity separation of the glycerol, thus adding more cost to the process.

Higher molar ratios result in greater ester conversion in a shorter time. Rapeseed oil was methanolyzed using 1% NaOH/KOH [46]. It was found that the molar ratio of 6:1 of methanol to oil gave the best conversion. When a large amount of free fatty acids was present in the oil, a molar ratio as high as 15:1 was needed under acid catalysis [47]. Freedman et al. [48] studied the effect of molar ratio (from 1:1 to 6:1) on ester conversion with vegetable oils. Soybean, sunflower, peanut and cotton seed oils behaved similarly and achieved highest conversions of 93–98% at a molar ratio of 6:1 [49]. In the ethanolysis of peanut oil, a 6:1 M ratio liberated significantly more glycerin than did a 3:1 M ratio [44].

In the process of alcoholysis, the catalyst, either sodium hydroxide or potassium hydroxide is dissolved in polar alcohol phase, in which triglycerides must transfer in order to react. The reaction is initially mass-transfer controlled and does not conform to expect homogeneous kinetics. When the concentration of these intermediates reaches a critical level, emulsions form. The larger non-polar group in ethanol, relative to methanol, is assumed to be the critical factor in stabilizing the emulsions. However, when the concentrations of mono- and di-glycerides are very low, then the emulsions become unstable.

2.3.3. The effect of catalyst

Catalysts are classified as alkali, acid, or enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed [48]. However if a glyceride has a higher free fatty acid contents and more water, acid-catalyzed transesterification is more suited [47,48]. Alkalis include hydroxide, methoxide, amide and hydride of sodium and potassium [47]. Sodium methoxide was more effective than sodium hydroxide [50] because of the assumption that a small amount of water was produced upon mixing NaOH and MeOH. Ester conversions at the 6:1 ratio of methanol/oil, for 1% NaOH and 0.5% $NaOCH_3$ were almost the same after 60 min [48]. Sodium hydroxide, however, is cheaper and is used widely in large-scale production. More recently, an immobilized lipase was employed to catalyze the methanolysis of corn oil in flowing supercritical carbon dioxide with an ester conversion of $>98\%$ [51].

Freedman et al. [48] found that sodium methoxide was more effective than sodium hydroxide because upon mixing sodium hydroxide with methanol a small amount of water will be produced, which will affect the product yield because of the hydrolysis reaction [52]. This is the reason why the catalyst should be added into the methanol first and then mixed with the oil. As the catalyst concentration increases the conversion of triglyceride and the yield of biodiesel increases since an insufficient amount of catalysts result in an incomplete conversion of the triglycerides into the fatty acid esters [53]. Usually, the yield reaches an optimal value when the catalyst (NaOH) concentration reaches 1.5 wt% and with further increase in catalyst concentration the yield decreases due to formation of soap [54].

Methanolysis of beef tallow was studied with NaOH and NaOMe as catalysts and NaOH was found to be significantly better than NaOMe [42]. The catalysts NaOH and NaOMe reached their maximum activity at 0.3% and 0.5% w/w of the beef tallow, respectively. Sodium methoxide causes formation of several by-products mainly sodium salts, which are to be treated as waste. In addition, high quality oil is required with this catalyst [55]. Attempts have been made to use basic alkaline-earth metal compounds in the transesterification of rapeseed oil for production of fatty acid methyl esters. The alkaline-earth metal hydroxides, alkoxides and oxides catalyzed reaction proceeds slowly as the reaction mixture constitutes a three immiscible phase system, which for diffusion reason inhibits the reaction [56]. The catalytic activity of magnesium oxide, calcium hydroxide, calcium oxide, calcium methoxide, barium hydroxide, and for comparison, sodium hydroxide during the transesterification of rapeseed oil was investigated. Sodium hydroxide exhibited the highest catalytic activity in this process. The degree to which the substrates were reacted reached 85% after 30 min of the process and 95% after 1.5 h, which represented a close value to the equilibrium. Barium hydroxide was slightly less active with a conversion of 75% after 30 min. Calcium methoxide was medially active. The degree to which the substrates were reacted was 55% after 30 min and the rate of reaction was slowest when catalyzed by CaO. Magnesium oxide and calcium hydroxide showed no catalytic activity in rapeseed oil methanolysis.

Acid catalyzed transesterification was studied with waste vegetable oils. The reaction was conducted at four different catalyst concentrations i.e., 0.5, 1.0, 1.5 and 2.25 M HCl in presence of 100% excess alcohol and the result was compared with 2.25 M H_2SO_4 and the decrease in viscosity was observed. H_2SO_4 has shown superior catalytic activity in the range of 1.5–2.25 M concentration [57].

Although chemical transesterification using an alkaline catalysis process gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several drawbacks: it is energy intensive, difficulty in recovery of glycerol, the removal of alkaline catalyst from the product, treatment of the alkaline waste water, and interference of free fatty acid and water in the reaction.

Enzymatic catalysts like lipases are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems, which can overcome the problems mentioned above [58]. In particular, the by-products, glycerol can be easily removed without any complex process, and also that free fatty acids contained in waste oils and fats can be completely converted to alkyl esters. On the other hand, the production cost of a lipase catalyst is significantly higher than others alkali or acid etc.

2.3.4. The effect of reaction time and temperature

The conversion rate increases with reaction time. Freedman et al. [48] transesterified peanut, cottonseed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60 °C. An approximate yield was 80% after 1 min for soybean and sunflower oils. After 1 h, the conversions were almost the same for all the four oils (93–98%). Ma et al. [42] studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to the mixing and dispersion of methanol into beef tallow. From 1 to 5 min, the reaction proceeded very fast. The apparent yield of beef tallow methyl esters surged from 1% to 38%.

Transesterification can occur at different temperatures, depending on the oil used. For the transesterification of refined oil with methanol (6:1) and 1% NaOH, the reaction was studied with three different temperatures [48]. After 0.1 h, ester yields were 94%, 87% and 64% for 60, 45 and 32 °C, respectively. After 1 h, ester formation was almost similar at 60 and 45 °C runs and was lower at 32 °C run. Temperature clearly influenced the reaction rate and yield of esters [20]. Leung and Guo [53] and Eevera et al. [54] found that when the reaction temperature increases beyond the optimal temperature, the yield of the biodiesel product decreases due to acceleration of the saponification reaction of triglycerides. Depending on the oil used, the optimal temperature ranges from 50 °C to 60 °C [20,48,53]. The reaction temperature must be less than the boiling point of alcohol in order to ensure minimum vaporization.

3. Catalytic transesterification

The transesterification of oils by catalyst are of two types, homogeneous and heterogeneous. The homogeneous catalysts have got more importance on industrial scale because these are more active, take less time for transesterification while heterogeneous catalysts are more useful for oils containing greater FFA contents. The merits and demerits of homogeneous and heterogeneous catalysts are summarized in Tables 3 and 6.

3.1. Homogeneous catalysts

Homogenous catalysts used for production of biodiesel are of two types, alkaline homogeneous catalyst and acid homogeneous catalyst. The alkaline homogeneous catalysts are suitable for virgin oil containing less FFA contents because high FFA contents cause saponification leading to soap formation and difficulty in separation. The acid homogeneous catalysts are more suitable for used cooking oil containing high FFA contents. The merits and demerits of alkaline homogeneous and acid homogeneous catalysts are summarized in Table 3.

3.1.1. Alkaline homogeneous catalysts

This class includes NaOH, CH_3ONa, KOH, and CH_3OK [48,59–68]. These catalysts are more economic because process is carried out at a low temperature (40–60 °C), less time (30–90 min) and under atmospheric pressure. Also the conversion rate is high with no intermediate steps. However, the alkaline homogenous catalysts are highly hygroscopic and absorb water from air during storage. They also form water when dissolved in alcohol and affect the yield [53]. Other merits and demerits are summarized in Table 3.

3.1.2. Acidic homogeneous catalyst

Acidic homogeneous catalysts include sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid [68,69]. These catalysts take more time and higher temperature for complete conversion as compare to alkaline homogeneous catalysts. The liquid acid-catalyzed transesterification process does not enjoy the same popularity in commercial applications as its counterpart, the

Table 3
Merits and demerits of homogeneous catalysts.

Type	Merits	Demerits	Ref.
Alkaline catalysts	• Low cost • Favorable kinetics • High catalytic activity, very fast reaction rate, 4000 times faster than acid-catalysts • Mild reaction condition and less energy intensive	• Requirement of low FFA • Anhydrous conditions • Saponification, if the FFA contents are more than 2 wt% • Low biodiesel yield due to emulsion formation • More wastewater from purification • Non-reusable	[63]
Acidic catalysts	• Insensitive for high FFA and water contents in the oil • Catalyze esterification and transesterification simultaneously • No soap formation • Preferred for low-grade oil • Reaction occurs under mild conditions and less energy intensive	• Very slow reaction rate • Equipment corrosion • More waste from neutralization • Recycling of catalyst is problematic • Weak catalytic activity • Higher reaction temperature • Long reaction times	[63]

Table 4
Use of homogeneous catalysts for transesterification of edible oil.

Oil	Catalyst	MeOH/ oil ratio	Catalyst conc.	Temp. (°C)	Reaction time (min)	% Yield	Ref.
Soybean	NaOH	6:1	–	60		80	[48]
	CH_3ONa	10:1	0.5	75	30	94	[73]
	NaOH	6:1	0.3	45	10–20	100	[74]
Sunflower	NaOH	6:1	0.5	60	–	80	[48]
	KOH	6:1	–	25	–	90	[75]
	KOH	6:1	1.3	25	60	98.4	[76]
Palm	NaOH	–	1.5	–	90	>95	[63]
Cottonseed	NaOH	–	1.5	–	90	90	[63]
	NaOH	6:1	0.5	60	–	80	[53]
	NaOH	6:1	1	60	120	90	[77]
	NaOH	6:1	0.75	65	120	96.9	[78]
Rice bran	NaOH	–	1.5	–	90	>90	[79]

base-catalyzed process. The fact is that the acid-catalyzed reaction is about 4000 times slower than the base-catalyzed reaction [70]. However, acid-catalyzed transesterifications hold an important advantage with respect to base-catalyzed ones: the performance of the acid catalyst is not strongly affected by the presence of FFAs in the feedstock. In fact, acid catalysts can simultaneously catalyze both the esterification and transesterification process. Thus, a great advantage with acid catalysts is that they can directly produce biodiesel from low-cost lipid feedstocks, generally associated with high FFA concentrations (low-cost feedstocks, such as used cooking oil and greases, commonly have FFAs levels of $\geq 6\%$). Recently, it has been shown how acid-catalyzed production of biodiesel can economically compete with base-catalyzed processes using virgin oils, especially when the former uses low-cost feedstocks [71,72]. The merits and demerits of alkaline and acidic homogeneous catalysts are summarized in Table 3.

3.1.3. Transesterification of edible oils by homogeneous catalyst

The edible oils like soybean, sunflower, palm, cottonseed, rice bran etc have been transesterified by many researchers which are listed in Table 4 [48,53,63,73–79] with conditions like, MeOH/oil ratio, catalyst ratio, temperature, reaction time and % yield.

It can be concluded from the data in Table 4 that more than 90% transesterification of edible oils to biodiesel can be achieved by optimizing the various parameters of the process i.e. methanol/oil ratio 6:1, catalyst concentration 0.5–1.5 w/w of oil, temperature 60 °C and reaction time of 90 min.

3.1.4. Transesterification of non-edible oils by homogeneous catalyst

The non-edible oils like pongamia pinnata, jatropha and neem have been transesterified by many researchers which are listed in Table 5 [54,80–83] with conditions like, MeOH/oil, catalyst ratio (w/w% of oil), temperature, reaction time and % yield. As in case of transesterification of edible oil, here too by optimizing the various parameters % yield can be obtained maximum.

3.2. Heterogeneous catalysts

Heterogeneous catalysts include both acidic and basic solids like MgO, CaO, Al–Mg hydrotalcites, La_2O_3, ZnO, CeO_2, $CaCO_3$, sulfated zirconium oxide, sulfated tin oxide etc. The merits and demerits of alkaline and acidic heterogeneous catalysts are summarized in Table 6 [66,84–88].

3.2.1. Transesterification of oils by heterogeneous catalysts

The edible oils like soybean, sunflower, palm, cottonseed, rapeseed etc., and non-edible oil like jatropha have been transesterfied by many researchers using various heterogeneous catalysts which are listed in Table 7 [73,76,89–105] with conditions like, MeOH/oil ratio, temperature, reaction time and % yield. These catalysts take more time, more methanol/oil ratio and higher temperature for complete transesterification.

4. Physico-chemical characterization of biodiesel

4.1. Physical characterization of biodiesel

The characteristics of biodiesel are close to mineral diesel and therefore biodiesel becomes a strong candidate to replace the mineral diesel if need arises. The conversion of triglyceride into methyl or ethyl ester through the transesterification process reduces the molecular weight to one-third that of the triglyceride, the viscosity by a factor of eight and increases the volatility marginally. Biodiesel has viscosity close to mineral diesel. The vegetable oil esters contain 10–11% oxygen by weight which may enhance combustion than hydrocarbon based diesel in an engine [106]. The cetane number of biodiesel is around 50. Biodiesel has lower volumetric heating values (about 10%) than mineral diesel but has the high cetane number and flash point. The esters have cloud and pour points that are 15–45 °C higher than those of mineral diesel.

The viscosity of a fluid can be expressed as dynamic viscosity and kinematics viscosity. Dynamic viscosity is measured in units

Table 5
Use of homogeneous catalysts for transesterification of non-edible oils.

Oil	Catalyst	MeOH/oil ratio	Catalyst conc.	Temp. (°C)	Reaction time (min)	% Yield	Ref.
Pongamiapinnata	NaOH	–	1.5	50	90	> 80	[54]
	KOH	10:1	1	105	90	92	[80]
	H_2SO_4	8:1	–	45	30	89.5	[81]
	NaOH	9:1	–	45	30	85	[81]
	KOH	6:1	1	65	120	98	[17]
Jatropha	NaOH	3:1	1	–	120–240	–	[82]
	H_2SO_4	0.28 v/v	1.4 v/v	60	88	99	[83]
Neem	NaOH	–	1.5	–	90	> 80	[54]

Table 6
Merits and demerits of alkaline and acidic heterogeneous catalysts.

Type of catalyst	Merits	Demerits	Ref.
Alkaline catalysts	• Relatively faster reaction rate than acid-catalyzed transesterification • Recyclable, high possibility to reuse and regenerate the catalyst • Reaction may occur under mild reaction conditions and less energy intensive • Fewer disposal problems • Higher selectivity • Noncorrosive environmentally benign • Longer catalyst lifetimes easy separation of catalyst from product	• Requirement of low FFA • Anhydrous conditions • More wastewater from purification • Requirement of higher molar ratio of alcohol to oil • High reaction temperature and pressure, diffusion limitations • High cost • Poisoning of the catalyst when exposed to ambient air • Soap formation if the FFA content in the oil is more than 2 wt% leading to decrease the biodiesel yield decreasing catalyst active sites may result to product contamination	[66,84–87]
Acidic catalysts	• Insensitive to FFA and water contents of oil • Simultaneous catalyzed esterification and transesterification • Preferred-method low-grade oil recyclable, easy separation of catalyst from product, eco-friendly	• Low acidic site • Low micro porosity • diffusion limitations • High cost, complicated catalyst synthesis procedures normally, higher reaction temperature, high alcohol to oil molar ratio and longer reaction time	[65,84,85,88]

Table 7
Use of heterogeneous catalysts for transesterification of edible and non-edible oils.

Oil	Catalyst	MeOH/oil ratio	Reaction time (h)	Temp. (°C)	% Yield	Ref.
Soybean	CaO, SrO	12:1	0.5–3.0	65	95	[89]
	MgO, ZnO, Al_2O_3	55:1	7	70, 100, 130	82	[90]
	MgO, Mg Al_2O_4	3:1	10	65	57	[91]
	WO_3/ZrO_2	40:1	20	200–300	90	[92]
	Zirconia-Al_2O_3 & Sulfated SnO,NaOH,SrO					
	Tungstated zirconia	12:1	0.5	65	90	[89]
	Sulfated zirconia oxide (SZO)	40:1	8	300	94	[92]
	Sulfated SnO	40:1	8	300	70	[92]
	Vanadium Phosphate	40:1	8	300	70	[92]
	Mg–Al hydrotalcite					
	KNO_3/Al_2O_3	40:1	1	150	80	[92]
	KI/Al_2O_3	15:1	9	65	67	[93,94]
	KF/ZnO	15:1	8	–	87	[95]
	KOH/ZnO	15:1	8	–	96	[96]
	CaO–La_2O_3	10:1	9	–	82	[97]
		10:1	9	–	74	[73]
		10:1	0.5	54	76	–
Palm	Mg–Al–CO_3 (hydrotalcite)	30:1	6	100	86.6	[98]
	ZnO	6:1	1	300	86.1	[99]
	ZrO	6:1	1	–	64.5	[99]
	ZrO_2/SO_4^{-2}	6:1	1	–	90.3	[99]
Rapeseed	Mg–Al hydrotalcite	6:1	4	65	70	[100]
Cottonseed	Mg–Al–CO_3 hydrotalcite	6:1	12	180–210	87	[93]
	TiO_2/SO_4^{-2}	12:1	8	–	90	[76]
	ZnO_2/SO_4^{-}	12:1	8	–	85	[76]
Sunflower	$NaOH/Al_2O_3$	48:6	1	50	99	[101]
	CaO	13:1	1.6	60	94	[102]
	Activated CaO	13:1	1.6	60	94	[102]
	Fe–Zn double metalcyanide complex	15:1	8	170	97	[103]
	$Ca(C_2H_3O_2)_2$	12:1	5	60	95	[104]
Jatropha	CaO	9:1	2.5	70	93	[105]

of centipoise. Kinematic viscosity takes into account the fluid density and is measured in units of centistokes. Viscosity affects the operation of fuel injection equipment, particularly at low temperature when increase in viscosity affects the fluidity of the fuel. Different instruments are used for the measurement of viscosity such as Ostwald viscometer, Ubbelohde viscometer etc. Biodiesel have viscosity close to diesel fuel. When the viscosity of biodiesel is higher, then fuel injectors do not operate accurately and do not spray fuel for burning properly. According to ASTM standard D6751 the acceptable viscosity range of biodiesel at 40 °C is 1.9–6.0 mm^2/s or cSt. The kinematic viscosities of various edible and non-edible oil biodiesels reported in literature are listed in Table 8 [59,60,77,78,107–117].

Density is an important parameter for the injection of diesel fuel into the system. It is desirable to maintain the diesel density within a tight tolerance limit to achieve optimum air to fuel ratios. Biodiesel have density in the range of 0.83–0.88 g/cm^3 [118]. The density of various edible and non-edible oil biodiesels reported in literature is listed in Table 8. The densities for most of the biodiesels are in the range of 0.880–0.889 g/cm^3 which are within limits of European standard (EN) 14214.

The acid number or neutralization number or acidity of biodiesel is the mass of KOH in milligram that is required to neutralize 1 g of a chemical substance. The acid number is the measure of the amount of carboxylic acid group in a chemical compound such as fatty acid or in a mixture of compounds. The acid number is used to quantify the amount of acid present for example in a sample of biodiesel. Biodiesel is composed of fatty acid methyl esters. It may also contain small amount of fatty acid, which are quantified by an acid number. The percentage of acid number in biodiesel greater than 3% causes operational problems such as corrosion and pump plugging by deposit formation, where as 0.5 g of acid number equalizes 1% free fatty acid. The transesterification would not occur if oil has free fatty acid content of $>3\%$ [119]. Acid number may be determined by acid–base titration using phenolphthalein as an indicator and isopropyl alcohol as a solvent. Non-edible oil contains more free fatty acids as compared to the edible oil. The literature data regarding acid number of various edible and non-edible oil biodiesels are listed in Table 8.

Cetane number is actually a measure of a fuel ignition delay; the time period between the start of injection and start of combustion of the fuel. In a particular diesel engine higher cetane fuel will have shorter ignition delay periods than lower cetane fuels. Cetane number is based on two compounds, hexadecane with cetane of 100 and heptamethylnonane with a cetane of 15. The cetane number scale shows that straight chain saturated hydrocarbons have higher cetane number as compared to the branched chain or aromatic component of similar molecular weight and number of carbon atoms. The cetane number varies from feed stock to feed stock, depending greatly on the chemical composition of the fuel and can affect engine's ability to start, the noise level and the exhaust emission. The cetane number of biodiesel from animal fats is higher than that of vegetable oil. The values of cetane number of soybean oil derived biodiesel ranges from 45 to 60 while those of rapeseed biodiesel ranges from 48 to 61.2 [120]. The ignition delay time of a fuel can be enhanced by compounds known as cetane improver. Cetane improvers have been identified for fatty acid compounds that occur in biodiesel. Cetane improver may have another important ramification, namely the reduction of NO_x exhaust emissions. It is known for petrodiesel that cetane improvers can reduce these exhaust emissions. Biodiesel of USA (ASTM D 6751), Germany (DIN V 51606) and European organization (EN 14214) has set this value as 47, 49, and 51, respectively [121]. The cetane numbers of various edible and non-edible oil biodiesels are listed in Table 8.

The flash point of a volatile liquid is the lowest temperature at which it can vaporize to form an ignitable mixture in air or flash point is the temperature at which the fuel becomes a mixture that will ignite when exposed to a spark or flame. Flash point of

Table 8
The physical properties of biodiesels.

Biodiesel source	Density (40 °C, g cm^{-3})	Kinematic viscosity (40 °C, mm^2 s^{-1})	Pour point (°C)	Cloud point (°C)	Acid number (mg KOH g^{-1})	Flash point (°C)	Cetane no.	Ref.
ASTM D 6751	–	1.9–6.0	−15 to 16	−3.0 to 12	0.5 max.	130 min.	47 min.	[41]
EN 14214	0.86–0.90	3.5–5.0	–	–	0.5 max.	120 min.	–	[38]
Cottonseed	–	5.10	−3.0	–	–	–	91.7	[77]
	–	4.02	–	–		–	55	[107]
	0.875	4.07			0.16		54	[78]
Canola	0.883	4.34	−8.0	–	0.16	107	–	
	0.889	3.53	–	–	–	–	56	[108]
Palm	0.880	5.7	–	13.0	–	164	62	[109]
	0.87(15)	4.4	15	15.2	0.08	182	58.3	[110]
Brassica alba	0.899	5.719	−6.0	2.0	–	140	–	[111]
Safflower	0.874	4.29	−8.0	−2.0	0.28	176	52	[112]
Sunflower	0.884	4.03			–		–	–
	0.860	4.6	–	1.0		183	49	[113]
	0.88	4.9	–	–	0.24	–	49	[60]
Soybean	0.885	3.97	0.0	–	0.16	139	–	
	0.883	5.75	–	–	0.45	168	56	[114]
	0.885	4.5 (37.8)	−7.0	1.0	0.20	178	45	[115]
	0.885	4.08	–	–	0.15	183	49	[113]
Rapeseed	0.880	4.15	−9.0	−3.0	0.37	165	51	[59]
	0.88	–	–	–	0.25	–	50	–
Pongamia pinnata	0.883	4.8	–	–	0.62	–	61	[116]
Jatropha	0.879	4.34	3.0	–	0.38	135	58.4	[117]
	0.863	4.78	–	–	0.49	–	61	[116]

biodiesel is greater than petrodiesel due to which it is safer in handling and storage than petrodiesel. Diesel flash point varies between 60 and 96 °C and biodiesel flash point range is between 130 and 170 °C. The flash points of vegetable oil methyl esters are much lower than those of vegetable oils. The flash points of various edible and non-edible oil biodiesels are listed in Table 8.

The temperature at which liquid becomes cloudy when it is cooled or temperature at which oil starts to solidify is known as cloud point. Biodiesel have high cloud point as compared to the high speed diesel. Cloud point of biodiesel depends upon the composition of the ester and ranges from −3 to +11 °C. When the temperature is very low biodiesel becomes solid which create problem in fuel filters and injector of engines. Although most of the biodiesel properties are comparable to the diesel fuel but the cloud point and pour point which indicate cold flow behavior of a fuel is very poor. In order to lower the cloud point of biodiesel, anti-gel additives such as ethanol, kerosene etc are being added into the biodiesel [122]. The cloud points of various edible and non-edible oil biodiesels are listed in Table 8.

The pour point of a liquid is the lowest temperature at which it will pour or flow under prescribed condition. It is the rough indication of the lowest temperature at which oil is readily pumpable. The pour point is always lower than the cloud point. Diesel and kerosene are common pour point additives that reduce the pour point gelling temperature significantly. The reported pour points of various edible and non-edible oil biodiesels are listed in Table 8.

4.2. Chemical characterization of biodiesel

Chromatographic and spectroscopic techniques are the most common analytical methods employed for the characterization of biodiesel.

4.2.1. Chromatographic techniques

The chromatographic methods being used for characterization of biodiesel include thin layer chromatography, high performance liquid chromatography, gel permeation chromatography and gas chromatography which are briefly discussed below.

4.2.1.1. Thin layer chromatography (TLC). The first method for monitoring the transesterification reaction of vegetable oils developed was thin layer chromatography (TLC) [48]. Besides fatty esters, this method allows to analyze tri- di-, and mono-glycerides. Moreover, the analysis time is quite short; 30 samples could be analyzed in 2–3 h. Moreever, this method shows lower accuracy and is sensitive to humidity. Moreover, the analysis is only qualitative and does not allow the exact determination of the extent of conversion [123,124].

4.2.1.2. Gas chromatography (GC). Gas chromatography (GC) has been the most used technique due to its high accuracy for the quantification of major and minor components. However, baseline drift, overlapping signals, and aging of standards and samples can drastically affect the GC accuracy. Flame ionization detection (FID) is the most widespread detector used in GC, but the utilization of mass spectrometer has increased. The latter eliminates any ambiguities about the identification of the eluting materials, but their quantification could be affected. Freedman et al. [48] developed the first GC methodology to monitor fatty acids, tri-, di-, and mono-glycerides in the transesterification reaction of soybean oil. In this method, before performing the analyses, mono- and di-glycerides have to be silylated with N, O-bis (trimethylsilyl) trifluoroacetamide (BSTFA). Such procedure affords the trimethylsilyl derivatives, allowing a better separation and tailing reduction. The authors used a short fused silica capillary column (1.8 m; 100% dimethylpolysiloxane), and tridecanoin as an internal standard. The complete separation of acylglycerols and fatty esters was obtained in a run time of 12 min. Cvengros and Cvengrosova [125–127] described a GC–FID method with a packed column to evaluate the conversion of rapeseed oil to fatty ethyl or methyl esters. The evaluation was performed through the peak areas of esters during the reaction. The advantages of this method were the requirement of already available compounds and the use of cheap columns. Mittelbach [128] and Boocock [129] also used GC for determination of composition of fatty acid methyl esters, mono, di and tri-glycerides using fused silica capillary column and DB-1 fused silica capillary column respectively.

The fatty acids composition of various edible and non-edible vegetable oil biodiesels is listed in Table 9 [76,130–136]. The soybean, sunflower cottonseed and safflower have greater unsaturated portion of C18:2 (carbon length and number of double bonds) while rapeseed oil has greater unsaturated portion of C18:1. The palm oil has almost equal composition of saturated portion C16:0 and unsaturated portion C18:1. The non-edible oil such as jatropha, neem and cannabis sativa linn have greater unsaturated composition of C18:1 and C18:2 while castor oil has 89.6% recinoleic acid.

4.2.1.3. High performance liquid chromatography (HPLC). HPLC analysis is less employed in biodiesel characterization, but the analysis time is shorter than GC and sample derivatization is not required. Moreover, this technique can be applied to biodiesel from different feedstock and is more appropriate for blend analysis than GC. Several detectors for HPLC biodiesel analysis are described, among them evaporative light scattering detection (ELSD) is quite suitable for biodiesel analysis.

The first HPLC method for monitoring transesterification was developed by Trathnigg and Mittelbach [137]. They described methodology with density detection (DD), which allows the determination of the overall content of tri-, di-, and mono-glycerides in biodiesel samples from methanolysis mixtures as well as the methyl esters detection. The analyses were performed through coupling cyano-modified silica with two-gel permeation chromatography (GPC)-columns, and using an isocratic eluent (chloroform/ethanol 0.6%). According to the authors, this method is simple and reliable HPLC with pulsed amperometric detection (the detection limit is usually 10–100 times lower than for amperometric detection and the detection limit is 1 μg/g) was used to determine the amount of free glycerol in vegetable oil esters. The HPLC–PAD method has proved to be simple, rapid and accurate [138]. The major advantage of this method is its high sensitivity. The simultaneous detection of residual alcohol is also possible with this technique [139].

In an extensive study [140] reverse phase high performance liquid chromatography (RP-HPLC) was used for the determination of compounds formed during the production of biodiesel from rapeseed oil with various detection methods: UV detection at 205 nm, evaporative light scattering detection (ELSD) and atmospheric pressure chemical ionization mass spectrometry (APCI-MS) in positive ion mode. The sensitivity and linearity of each detection method varied with the individual triglycerides. ELSD and APCI-MS have decreased sensitivity with increasing number of double bonds in the fatty acid methyl esters. However, the sensitivity of UV detection varies with individual triglycerides. APCI-MS is stated to be the most appropriate detection method for the analysis of biodiesel. HPLC method of quantification of mono-, di-, tri-glycerides and esters using UV detection method at the region of 205 nm was studied for methanolysis of rapeseed oils [141]. An HPLC equipped with a refractive index detector was use for the analysis of biodiesel produced from soybean oil [67].

Table 9
Major fatty acid composition (%) of biodiesels.

Biodiesel	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	Ref.
Soybean	13.9	0.3	2.1	23.2	56.2	4.3	[130]
	14	–	4.0	24	52	–	[76]
	12	–	3.0	23	55	6.0	[131]
	–	11.75	3.15	23.26	55.53	6.31	[132]
	11.6	0.3	4.2	21.6	53.7	7.5	[133]
Rapeseed	3.5	–	0.9	64.1	22.3	8.2	[130]
	3.0	–	1.0	64.0	22.0	8.0	[131]
	–	3.49	0.85	64.4	22.3	8.23	[132]
Sunflower	6.4	0.1	2.9	17.7	72.9	–	[130]
	6.0	–	3.0	17.0	74	–	[131]
	5.5	0.1	4.7	19.5	68.5	0.1	[133]
	–	6.08	3.26	16.93	73.73	–	[132]
Cottonseed	22.96	0.9	2.3	16.7	55.4	0.2	[131]
	28.7	–	0.9	13.0	57.4	–	[130]
	27.3	0.8	2.0	18.3	50.7	–	[133]
	28.33	–	0.89	13.27	57.51	–	[132]
Safflower	7.0	–	2.0	12.0	78	–	[131]
	7.3	–	1.9	13.6	77.2	–	[132]
Palm	43.7	0.1	4.5	39.8	10.5	0.3	[133]
	42.6	0.3	4.40	40.5	10.1	0.2	[131]
Jatropha	15.6	–	9.7	40.8	32.1	–	[134]
Neem	13.6–16.2	–	14.4–24.1	49.1–61.9	2.3–15.8	–	[135]
Cannabis sativa linn	–	–	–	15.0	65.0	15.0	[130]

4.2.2. Spectroscopic techniques

The spectroscopic techniques include nuclear magnetic resonance (NMR) and infrared spectroscopy which are being used for chemical characterization of oil and biodiesel. These are briefly discussed below.

4.2.2.1. Nuclear magnetic resonance (NMR). Spectroscopic analyses are most employed for monitoring the transesterification reaction and for the determination of blend level. Nuclear magnetic resonance (NMR) spectroscopy is an excellent technique, but the instrumentation and maintenance costs are relatively high. The method is quicker and simpler than GC and HPLC. Gelbard et al. [142] described the utilization of nuclear magnetic resonance, particularly ^{1}H NMR, for monitoring the yield of transesterification reaction for the first time. The peaks of methylene group adjacent to ester moiety in triacylglycerols (α-CH_2, 2.3 ppm, t) and the methoxy group in the esters (OCH_3, 3.7 ppm, s) were used to follow the reaction progress. The conversion was calculated from the areas of these peaks, using an equation:

$$C = 100\frac{2A_{Me}}{3A_{CH_2}}$$

where C is the percentage conversion of triglycerides to corresponding methyl esters; A_{Me} is the integration value of the methoxy protons of the methyl esters and A_{CH_2} is the integration value of α-methylene protons.

This method is faster and simpler than chromatographic ones. However, instrumentation and maintenance costs are relatively high and must be evaluated. Moreover, a small amount of sample is required and it could be analyzed without a pre-purification process. The ^{1}H NMR method to monitor the transesterification reaction of soybean oil was also developed and used to establish the average degree of fatty acid unsaturation and methyl esters in biodiesel [143]. ^{1}H NMR methodology to monitor the ethanolysis as well as to quantify the content of fatty ethyl esters in mixtures of biodiesel and oil was also developed [144]. The region of 4.05–4.40 ppm (ester ethoxy and glycerol methylene hydrogens) was chosen for the quantification of the reaction.

The use of ^{13}C NMR for monitoring the transesterification has also being used [145]. The signal at 14.5 ppm of the terminal methyl groups, which are not affected by reaction, was chosen as internal standard, and the glyceridic carbons at 62–71 ppm along with methoxy carbon of fatty esters at 51 ppm were selected to determine the conversion rate.

4.2.2.2. Infrared spectroscopy (IR). Infrared spectroscopy is another technique for monitoring the transesterification of oils/fats. The first reported work was by Knothe [146,147] who developed a fiber-optic near infrared (NIR) method to monitor the transesterification reaction of soybean oil, which was based on the differences in the NIR region at 6005 and 4425–4430 cm^{-1}, where fatty esters display peaks and triglycerides exhibit shoulders, respectively. Thus, these peaks were chosen for monitoring the reaction. In fact, the former peak was used for quantification since it is more suitable. Besides the transesterification monitoring, the biodiesel quality can also be assessed through this methodology by the correlation with other analytical data. This kind of procedure is a way to cross-check the results. In addition, the NIR method can also be used for the quantification of methanol in biodiesel, which can be an alternative to flash point evolution of biodiesel. The NIR method could be used to monitor the reaction of several oils as well as to ensure the quality control of biodiesel when employed with other analytical techniques. The use of FT-IR method with a multivariate approach (PLS, partial least squares regression) has been used to monitor the ethanolysis of degummed soybean oil by using the ester peak at 1700–1800 cm^{-1} [148]. Such a method was considered to be fast and accurate to predict reaction yields. Later, Siatis et al. [149] developed FT-IR method to monitor the ultrasonically assisted extraction transesterification of seed and seed cakes from cotton, sunflower, sesame, and cynara cardulus seeds. The method affords the

simultaneous determination of fatty acid methyl ester and triglycerides. PLS algorithm and 1300–1060 cm^{-1} spectral region were used to determine the percentage of fatty ester in the mixture of reaction. The most characteristic peak at 1200 cm^{-1} is that related to O–CH_3 vibrations in the methyl fatty esters. Subsequently, Ghesti et al. [150] described a FT-Raman spectroscopic method to monitor and quantify the transesterification of soybean oil. The differences between the Raman spectrum of vegetable oil and the fatty ethyl esters were observed in bands at 2932 cm^{-1} (νCH2), 861 cm^{-1} (νRCO and νC–C), 372 cm^{-1} (δCO–O–C), as well as by the displacement of the C=O band from 1748 to 1739 cm^{-1}. To build analytical curves and to check the method, uni- and multi-variate analysis methods were also employed. Using an internal normalization standard νCH band, the best results were achieved by Raman/PLS calibration models. The method was correlated with a new NMR technique developed for monitoring the ethanolysis of soybean oil that could be extended to the transesterification of other vegetable oils [151]. Recently FT-IR method has been described to assess the extent of transesterification reaction of oils in which methyl peak areas/intensities and positions could be employed to monitor the reaction [152]. Finally, mid-IR with a multivariate approach was used to monitor on line the transesterification of soybean oil with ethanol by using a cylindrical reflectance cell of PbSe and the range of 3707–814 cm^{-1} were employed [153]. The monitoring was carried out for 12 min. The proposed method could be used in the process control and for reaction optimization since it is fast and shows low-cost. Dubé et al. [154] suggested two distinct methods for monitoring the biodiesel production from waste canola frying oil: GPC with refractive index detector (RID), and attenuated total reflectance (ATR)–FT-IR spectroscopy. The decreasing of the peak at 1378 cm^{-1} (terminal methyl and OCH_2 in acylglycerols) in the ATR–FT-IR spectrum was used for monitoring the biodiesel synthesis. The results of the analyses of 100 biodiesel samples by both methods showed very small differences. Thus, the authors considered that the methodologies could be equivalent. However, the GPC–RID methodology allows only the quantification of monoglycerides and fatty methyl esters, while the ATR–FT-IR just consents the quantification of total glycerides. Arzamendi et al. [155] reported a method based on size exclusion chromatography to determine simultaneously the total amount of tri-, di-, monoglycerides, fatty acid methyl esters, free glycerol and methanol in samples from the transesterification reaction of sunflower oil. The method is simple, robust, relatively fast, it may be conducted at room temperature and it gives accurate and reproducible results.

5. Conclusion

Biodiesel have been synthesized from various edible and non-edible oil sources by transesterification process. The production of biodiesel (1st generation biofuel) mainly from edible oils have been criticized due to possible future shortage of food, therefore, the recent research is being focused on production of biodiesel from non-edible oils (2nd generation biodiesel) such as jatropha, jojoba, *pongamia pinnata*, neem etc. It will be a better option to produce biodiesel from non-edible oils to minimize the risk of food shortage.

The membrane extraction process for the separation and purification of biodiesel is better than the conventional processes because it yields high purity biodiesel but at the higher cost.

The transesterification process is affected by various parameters such as methanol/oil ratio, effect of temperature, effect of catalyst concentration and time required for complete transesterification. The alcohol to oil ratio is a very important parameter because it effect the % age conversion of triglycerides to fatty acid methyl esters (FAMEs). It is found that as alcohol (methanol) concentration increases, the % age conversion also increases up to a specific limit and beyond which it decreases due to emulsification. In case of edible oils, the molar ratio of 6:1 (methanol:oil) has been optimized and reported by many authors while in case of non-edible oils, more alcohol concentration is required to get better yield. The type and concentration of catalyst is a key parameter which affects the % age conversion of triglycerides into fatty acid methyl esters. Among the base, acid and enzyme catalysts, base catalyst have been found to be the best especially in edible oils with low FFA contents and has been reported frequently. The % age conversion of oil to biodiesel is directly proportional to the concentration of catalyst and temperature up to a specific limit, beyond which it decreases due to saponification especially in case of base catalysis. The optimized transesterification temperature of 60 °C gave the best conversion results. It is important to note that all the mentioned parameters are dependent on the nature of oils (edible or non-edible oils) and should be optimized accordingly.

The nature of catalyst used in transesterification depends on nature of oils. The homogeneous base catalysts are best suited for oils with low FFA contents due to their rapid transesterification and low cost. The homogeneous acid catalysts are best suited for waste cooking oils and non-edible oils which contain high FFA contents. The transesterification by heterogeneous catalysts is more time consuming and requires higher alcohol to oil ratio. But these catalysts are reusable by reactivation, are non-corrosive and eco-friendly.

The synthesized biodiesel can be characterized by various physico-chemical parameters such as kinematic viscosity, density, cloud point, pour point, flash point, cetane number and acid number, which are in accordance with the ASTM D 6751/ EN 14214 standards except that of flash point which is higher than the fossil diesel. This results in a relatively inability of the biodiesel to combust desirably in the compression ignition engine in comparison to fossil fuel and could be overcome by appropriate blending with fossil diesel.

The chemical characterization is performed by chromatographic and spectroscopic techniques which provide quick analysis of fatty acid composition and quality of biodiesel. ^{1}H NMR was proved to be a good technique to calculate % age conversion of triglycerides to fatty acid methyl esters. The gas chromatography has been found to be the preferred technique to find out composition of fatty acid methyl esters and check the intermediates by identifying mono-, di- and tri-glycerides in the samples of fatty acid methyl esters.

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